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INFLUENCE OF CURE ENVIRONMENT AND CURE TEMPERATURE ON FAILURE PROPERTIES OF ACETYLENE TERMINATED SULFONE

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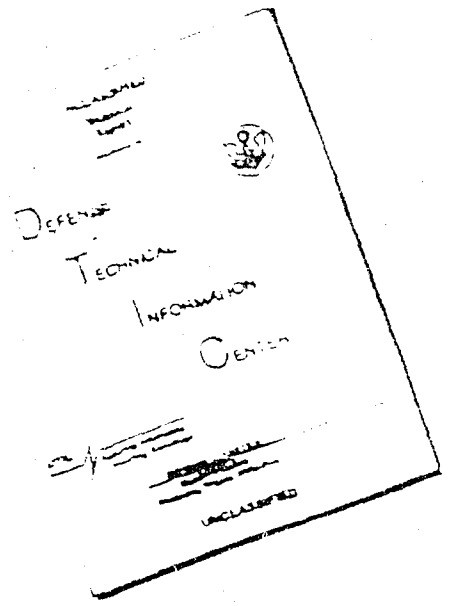

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Air cure effects on the tensile and fracture behavior are studied with an acetylene terminated sulfone resin. It is found that in all instances, the air cure improves the mechanical properties. As much as 30% improvement can be attained depending on the extent of cure performed in the presence of air. The amount of improvement appears to depend on the thickness of the test specimens. Density measurements show different values for the air cure and the nitrogen cure specimens. Similar thickness dependency on the total air effect is also observed. The air effect is also affected by the stage of cure when the air

20. Abstract (Continued)

is introduced. The effect is larger when air is introduced early in the cure. The results are consistent with the dynamic mechanical data and show the role of air diffusing into the sample in controlling the total improvement in mechanical properties. Tensile properties at different extents of cure are also measured. Those data indicated that at the initial cure stages, the mechanical properties of the resin are poor. Thus damage could be sustained by parts during the processing procedure if they were not handled properly at these stages.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2419, "Nonmetallic and Composite Materials, Task No. 241904, Work Unit Directive 24190415, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. F. E. Arnold as the AFWAL/ML Project Scientist, Co-authors were Dr. C. Y-C. Lee, Materials Laboratory/AFWAL/MLBP and Drs. C. C. Kuo and N. C. Lee, visiting Scientists.

This report covers research conducted from September 1981 to December 1981.

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SECTION I

INTRODUCTION

Acetylene terminated (AT) resins can cure thermally without giving off volatiles. Its high temperature properties and moisture insensitivity have made the AT technology a promising approach to attain high use temperature thermosetting systems (Reference 1).

Recent studies of the dynamic mechanical responses of the AT resins have shown that curing the resins in the presence of air can change the post cure kinetic rate and depress the glass transition temperatures of the fully cured systems (References 2, 3). The data strongly suggest that the cured chemical structure or the network was changed when the resin was cured in the presence of air. The intent of this study is to see if the curing in the presence of air can cause changes in the mechanical properties of the resins.

Mechanical properties of the ATS at different extent of cure were also measured. The different extents of cure were chosen to reflect the different stages in the composite cure schedule. This will allow a preliminary probe into the development of the mechanical properties during the cure cycle.

SECTION II

EXPERIMENTAL

The resin used in this study has a sulfone structure (Reference 4) between the terminal acetylene groups. The air curing effect on the dynamic mechanical response of this resin was studied with torsion impregnated cloth analysis and was reported elsewhere (Reference 3).

The mechanical test specimens were prepared by precuring the resin in silicone molds. The resin was degassed under vacuum at 120°C for 70 minutes before being poured into the mold. The resin was cured in the close-faced mold for 45 minutes at 150°C. This precuring was required to pre-shape the resin in the dog-bone shape for tensile testings, or the bar shape for fracture toughness testings. Then the specimens were removed from the mold and were exposed to either air or nitrogen environment during the cure.

The tensile testings were done using dog-bone specimens with gage-lengths of about 1½ in., sample widths of about 3/16 in. and thickness of 20 mil. The experiments were done using an Instron Tester.

The elongation at break values were calculated from the recorded load-displacement curve. The recording chart speed and the Instron crosshead travel speed were calibrated; and they were used to calculate the strain. Recent comparison of strain measurement using this method with actual extensometer measurement indicate that for thin ATS samples ($\sim$20 mil), there is practically no discernable difference between the two methods of measurement. However, with thicker samples or tougher resin, which increase the load into the 50 lb range, as much as 20% difference due to instrument compliance has been observed.

In spite of this factor, the data reported here are still valid for relative comparison of properties within a series of samples. The absolute values, however, should be used with caution.

The fracture toughness (K_Q) testing procedure has been outlined elsewhere (Reference 5). The specimens used were ½ in. compact tension specimens with thickness of 1/8 in. The crack averaging method reported by Lee and Jones (5) was used to calculate crack lengths (Reference 5). The load-unload-reload cycle was used to obtain multi-fracture calculations from each specimen. Because of the size of the specimen, the calculated value is designated as K_Q rather than K_{1c}.

The density measurements were made with a density gradient column as outlined in ASTM D-1505 (Reference 6).

SECTION III

RESULTS AND DISCUSSIONS

1. TENSILE TESTINGS

Specimens were cured to different extents of cure, using different curing cycles. The cure cycles were identified alphabetically and are listed in Table 1. By assuming that the gelation peaks observed in the isothermal experiments of torsion impregnated cloth analysis being the same cure state, these cure histories can be represented on the time-temperature-transformation (TTT) diagram (Reference 7) of the sulfone resin reported by Kuo and Lee (Reference 3). They are shown in Figure 1.

The tensile strength data from specimens at different extents of cure are shown in Figure 2. Spectroscopic data have shown that the cure state of the terminal acetylene reaction cannot be represented simply by a single parameter like percent of acetylene conversion (Reference 8). Works are currently underway to find a multi-parameter approach to describe the cure state. At the present time, the cure states are just represented arbitrarily in increasing extent of cure in alphabetical sequence.

Figure 2 shows that all the cure data have higher values than the corresponding nitrogen cure. The tensile strength increases initially with increasing extent of cure. The air cure data appear to have reached a constant value after state C. For the nitrogen data, the value at state E decreases. The improvement of properties increases with increasing extent of cure.

It has been shown that the presence of air slows down the cure kinetics. The data here also suggest that the tensile strength improves with higher extent of cure. So the improvement in properties cannot be accounted for by the difference in extent of cure due to different cure kinetics. Air must have influenced the cure chemistry and caused the formation of a different network structure which was responsible for the properties changes.

TABLE 1

CURE CYCLE FOR DIFFERENT EXTENT OF CURE

CURE STATE	CURE HISTORY
A	150°C/45min. (in mold)
B	A + 170° C/45 min. (Air/N_2)
C	A + 200° C/45min. (Air/N_2)
D	A + 250° C/45min. (Air/N_2)
E	B + 250°C/4 $\frac{1}{2}$ hr. (Air/N_2)
F	B + 250° C/20hr. (Air/N_2)

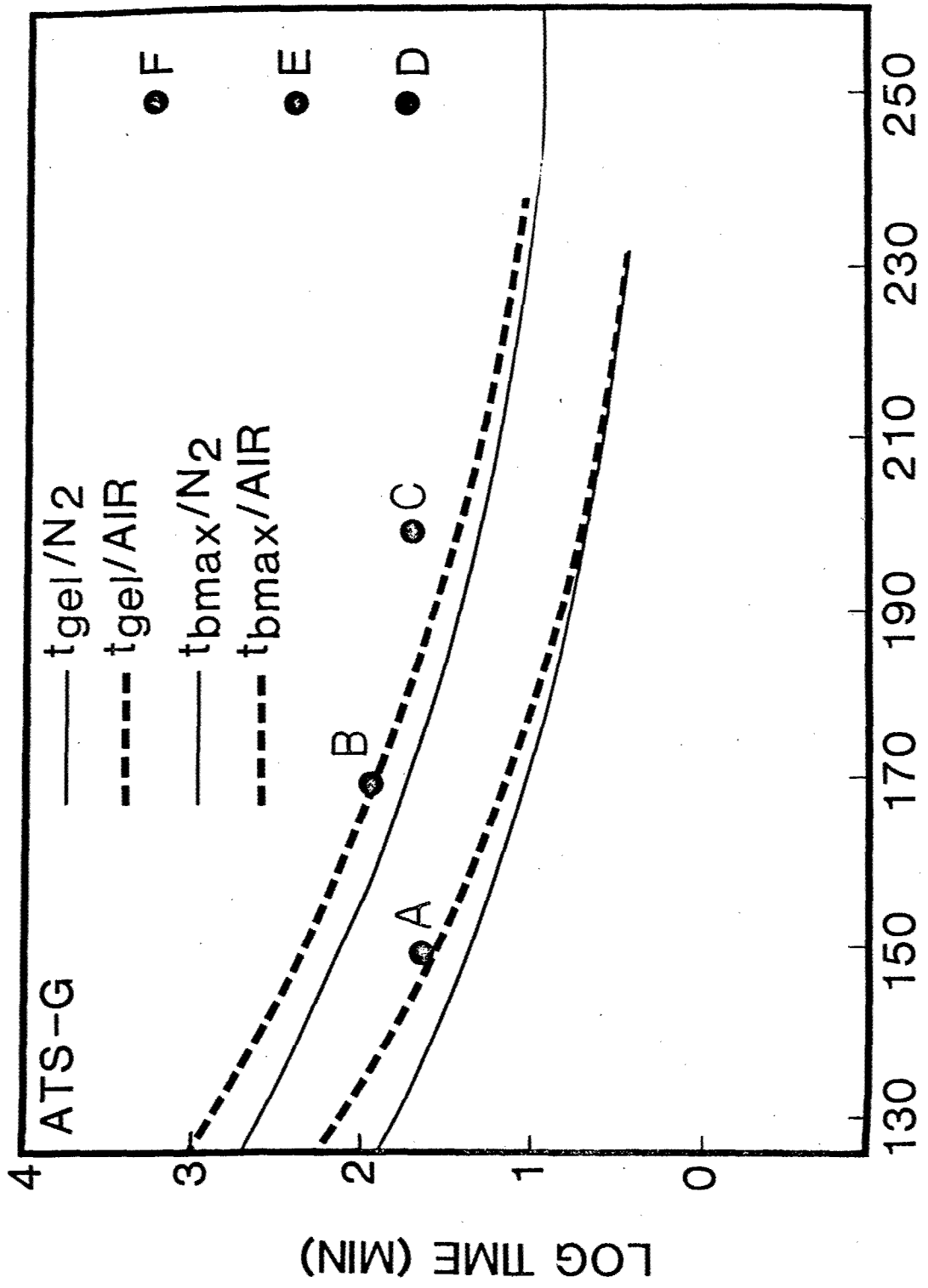

Figure 1. Representation of the Cure States on the Time Temperature Transformation Diagram

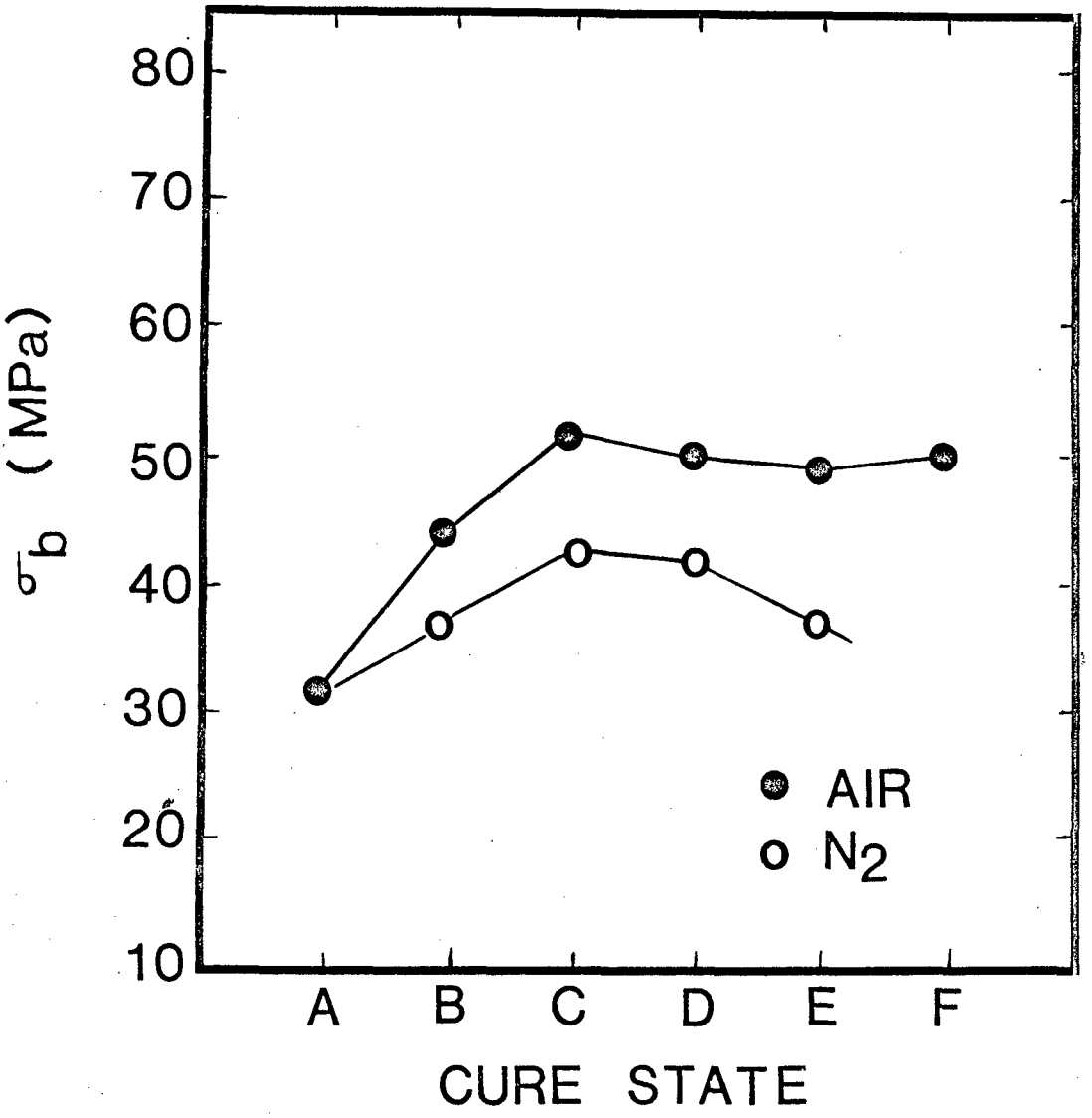

Figure 2. Plot of Tensile Strength vs Cure States

The torsion impregnated cloth analysis results of the sulfone resin showed the degradation effect at high temperature when the experiment was conducted in nitrogen environment. In the presence of air, the oxidative crosslinking effect masked out the degradation effect. This could have explained the different trends in tensile strength at the higher extent of cure. The nitrogen cure data may be showing the degradation effect. For the air data, either the oxidative crosslinking slows down the degradation, or its net effect compensates for the properties loss due to degradation.

Figure 3 shows the elongation at break data. Again, the air cure data are consistently better than the nitrogen cure data. However, the nitrogen data do not show the kind of decrease at high extent of cure as in the tensile strength data. This is reflected in the initial modulus plot shown in Figure 4. In both the nitrogen and air data, a sudden change in modulus occurs at a certain extent of cure. This change in modulus makes the tensile strength of state E (nitrogen cure) to decrease without a corresponding decrease in elongation at break. This change in modulus may reflect the temperature effect on the cure mechanism.

Another plausible explanation for the decrease in properties at the higher extent of cure is that the network formed at the later stages of cure is "too-tightly" crosslinked. They will cause a decrease in the elongation at break. However, in such an instance, one would expect the modulus to increase. The data here do not appear to agree with this expectation.

2. FRACTURE TOUGHNESS TESTINGS

In all cases, the air cure fracture toughness (K_Q) data are consistently better than the nitrogen cure data. The extent of improvement however are less than that from the tensile data. This can be due to the sample thickness effect which will be explored further in a later section.

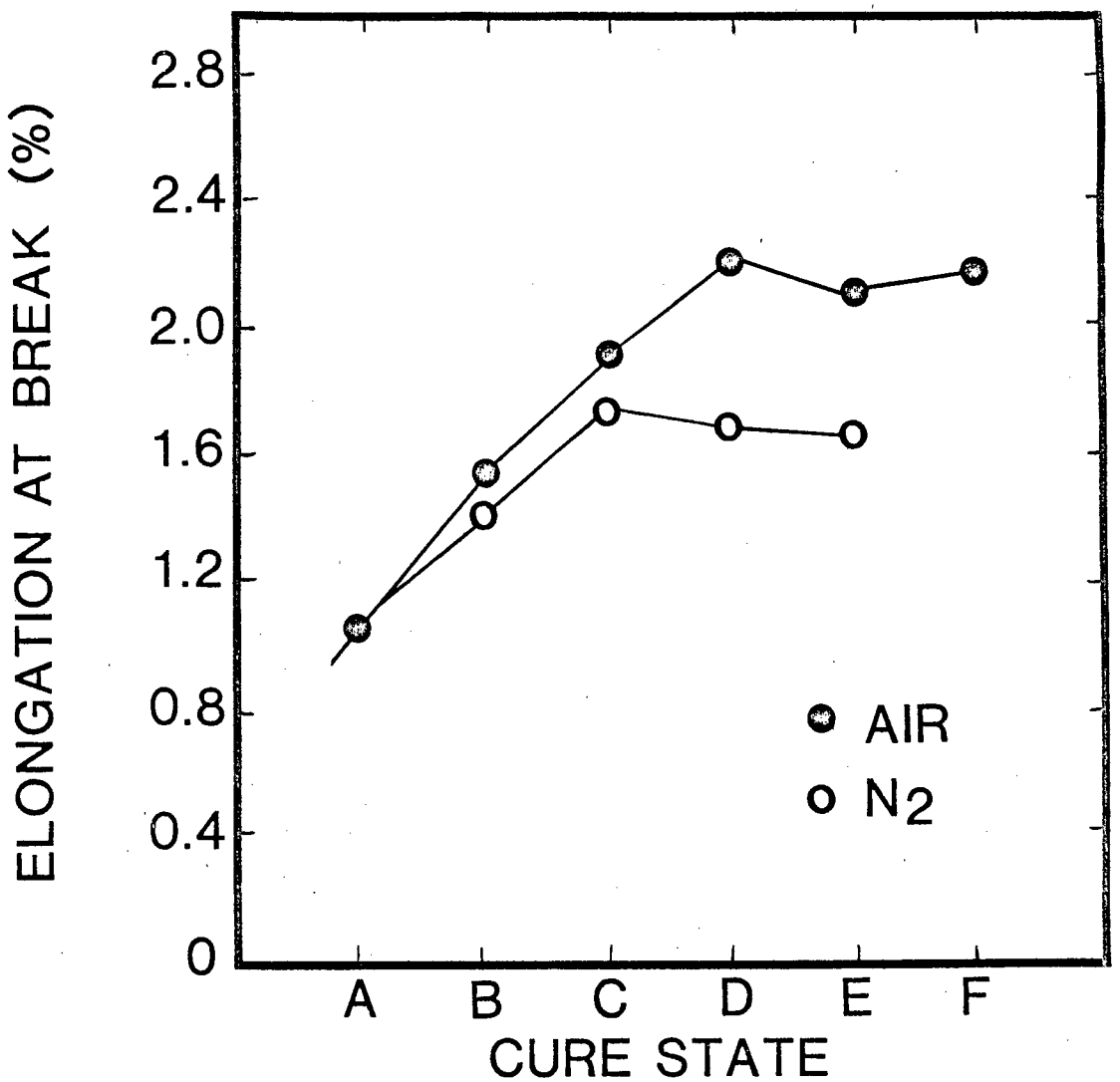

Figure 3. Plot of Elongation at break vs Cure States

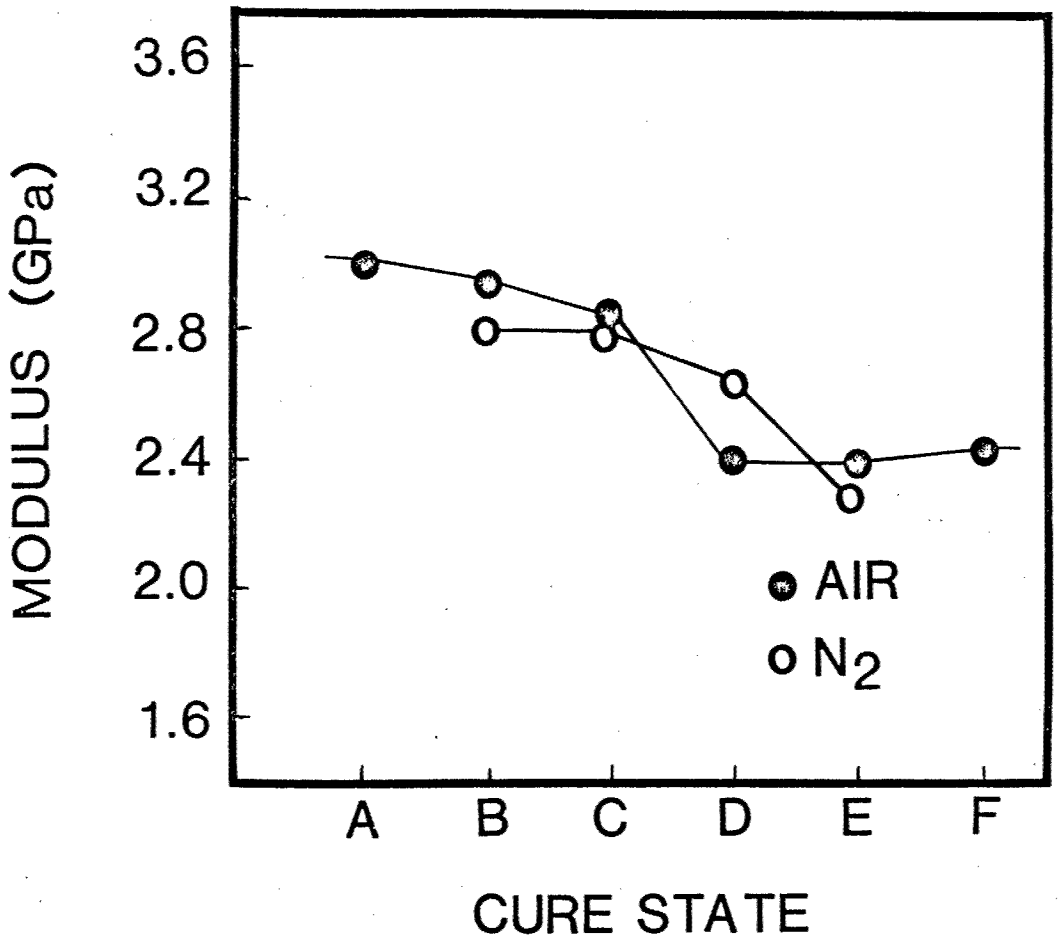

Figure 4. Plot of Initial Modulus vs Cure States

An attempt was made to test the effect of the sequence of air exposure on the mechanical properties. Samples with cure state E were used for this testing. After the removal from the molds, the samples were cured twice in this particular cure history: first, at 170°C for 45 minutes; then at 250°C for 4 1/2 hrs. An air or nitrogen curing environment was used at these two steps of cure. The data are listed in Table II in a matrix format. The columns indicate the cure environment and the rows indicate the post-cure environment. It is clear from the matrix that air data are better than the corresponding nitrogen data.

The data also show that the air effect may be more significant at the early cure stage than in the post cure stage. The difference in values is greater between columns than between rows. In light of the possibility of having degradation effect on the tensile properties, it is not clear how much of the difference observed is accountable to degradation of the resin. From a practical standpoint, the data show the advantage of exposing the specimens to the air environment at an early stage of cure.

3. DENSITY MEASUREMENT

Densities of specimens from different cure states were measured with a density gradient column. The results are plotted in Figure 5. In all cases, the air cured samples have a higher density than the nitrogen cured samples. Again, the difference in density between the air and nitrogen samples increases with increasing extent of cure.

One possibility for the density of the air cured specimens to have a higher value is that they may have larger volume shrinkage. However, equally plausible is that the weight of the sample may have increased. High temperature isothermal TGA (Thermal Gravimetric Analysis) data of several acetylene terminated systems in air environment have indicated an initial weight gain prior to degradation (Reference 9). Curing in air could have increased the sample weight also if oxygen is coupled into the curing reaction and becomes part of the reacted molecular structure. The largest increase in density reported here is about 0.5%. If all the density increase is due to weight gain, it is roughly estimated that an oxygen atom is gained for every five sulfone resin molecules.

TABLE 2

SULFONE RESIN CURE SEQUENCE EFFECT

K_o CALCULATION

MPa- $\sqrt{m}$

POST CURE (250°C)	CURE (170°C) N_2	CURE (170°C) AIR
N_2	.344	.374
AIR	.359	.376

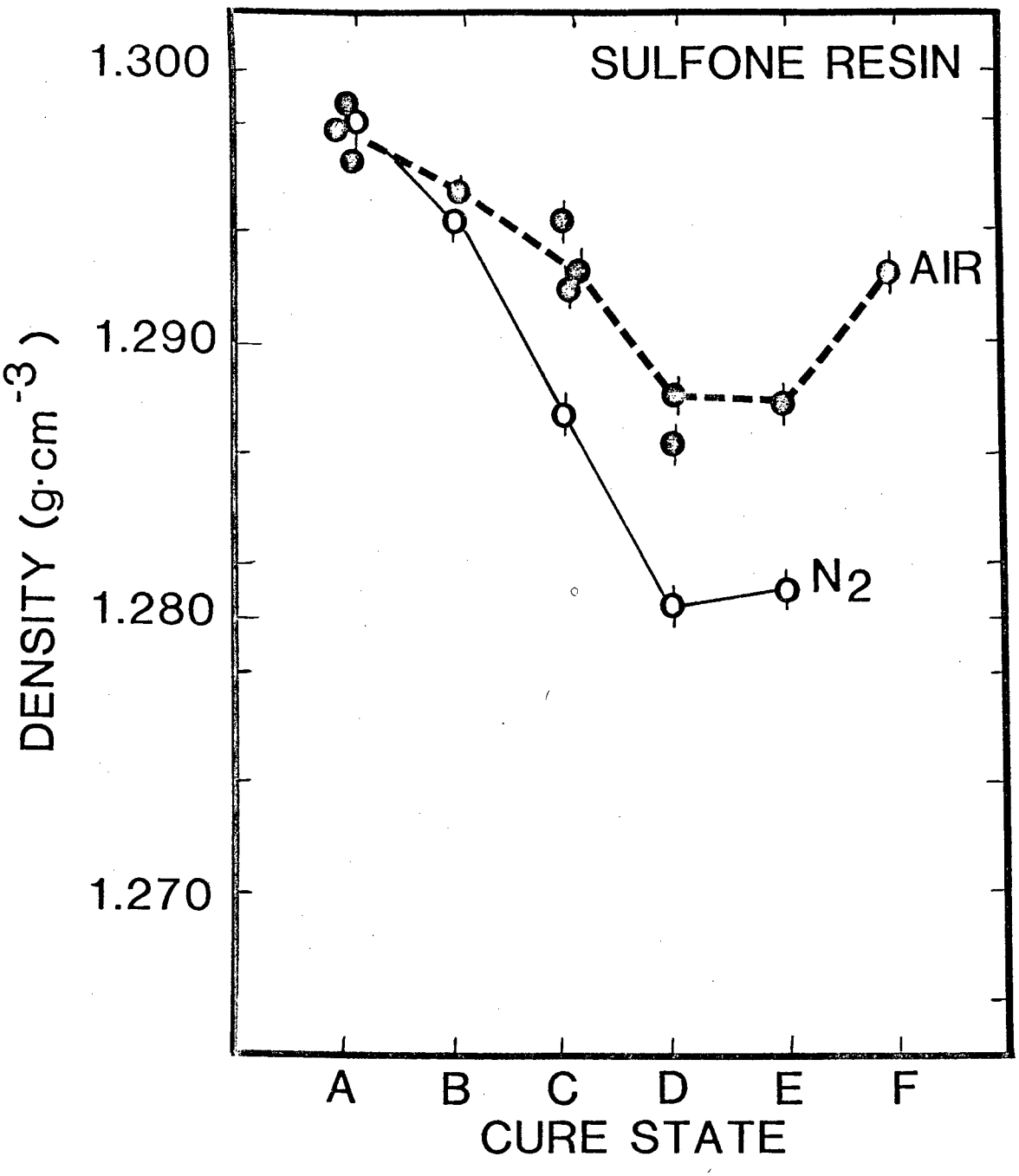

Figure 5. Density of the Resin at Different Extent of Cure

All densities reported here are higher than the uncured resin density. This increase in density can be attributed to the volume shrinkage of the resin as the material cured from a liquid state to a solid state through gelation and vitrification. Both the air and nitrogen data reported here also show an initial decrease in density with increasing extent of cure, then level off at about state D. The data suggest an increase in volume with additional cure in the solid state, or a weight loss during the early stages of cure.

It is not sure which factor is responsible for the density decrease, but similar results have been observed with another acetylene terminated resin with a quinoxaline backbone (Reference 10). The density measurements from an isothermal cure experiment indicated an increase in density prior to vitrification, the density decreased after the vitrification point.

The decrease in density seems to have stopped between state D and E. This could have been related to the modulus changes shown in Figure 4.

4. SAMPLE THICKNESS EFFECT

Both the tensile data and fracture toughness data show that curing in air can improve the mechanical properties of the resin. However, the tensile data show 20 to 30% increase in properties, but the K_Q values show only around 10% increase. The cause is suggested in a previous section as a sample thickness effect.

Torsion impregnated cloth analysis data (3) have shown that factors controlling the amount of air diffusing into the sample will influence the total air effect (Reference 3). Likewise, sample thickness should be another variable that will influence the total air effect.

Specimens with thickness of 20 mil, 30 mil and 40 mil were prepared and their densities were measured. The data are shown in Figure 6. Four sets of data are shown. The data labelled as A and E/N_2 corresponds to cure state A and cure state E cured under nitrogen environment. There is practically no thickness dependency in these data. The other two sets of

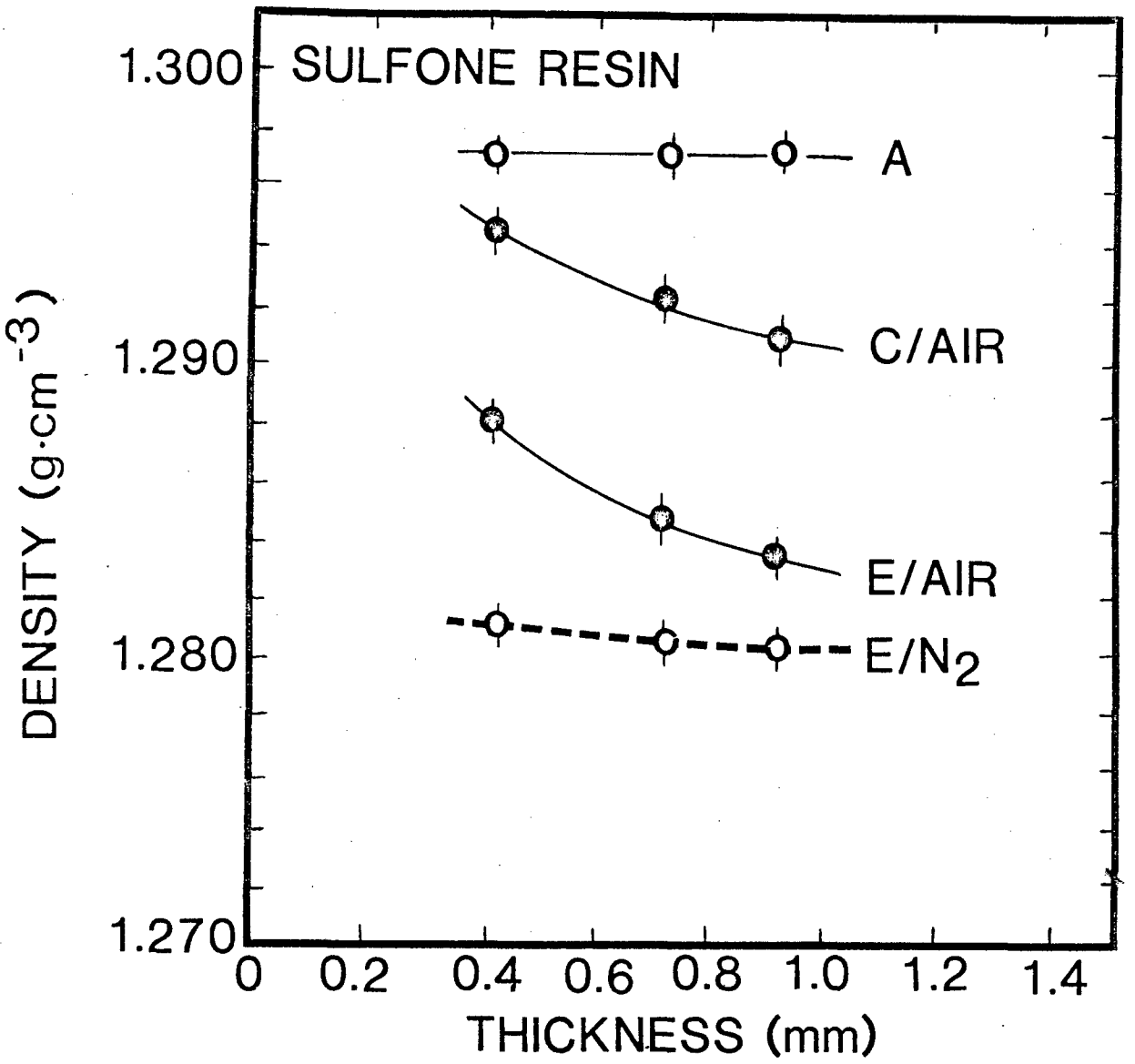

Figure 6. Sample Thickness Effect on Density Measurement

data represent the cure state C and cure state E in air environment. The thickness dependence is obvious. Comparing with Figure 5, it is reasonable to say that the total air effect decreases with increasing sample thickness.

The tensile strengths of specimens with cure state F are also plotted as a function of sample thickness and are shown in Figure 7. Again, the total improvement in mechanical properties through the air cure is shown to be influenced by the sample thickness. The trend observed is in good agreement with the density data.

5. MECHANICAL PROPERTIES AT DIFFERENT CURE STAGES

Figure 8 shows the elongation at break data of ATS as a function of cure time at 140°C. The open circles indicate the properties cured only at 140°C; and the closed circles indicate the values for similar cure histories with an additional post cure condition which was 5 hours at 250°C.

It is obvious that the post cure condition improves the properties of the resin. The values without the post cure are very poor. The data also show improvement of the properties with increasing cure time; but even after 20 hours of cure the value is lower than the post cure values. After the post cure, the properties are very similar regardless of the precure histories. Although a slight positive correlation with increasing precure time can be discerned from the data, the total range of variation is small in comparison with the improvement from the post cure condition.

These data seem to imply that precuring condition is not a significant factor to consider in designing a proper cure cycle for the resin. However, if the parts under fabrication were handled before the final post cure was completed, then the precure condition can be a significant factor. If the parts were handled before adequate properties were developed, they could be damaged with microcracks which may or may not be repaired by the post cure condition. There are reports that certain ATS prepreg (angle-plies) samples were found to

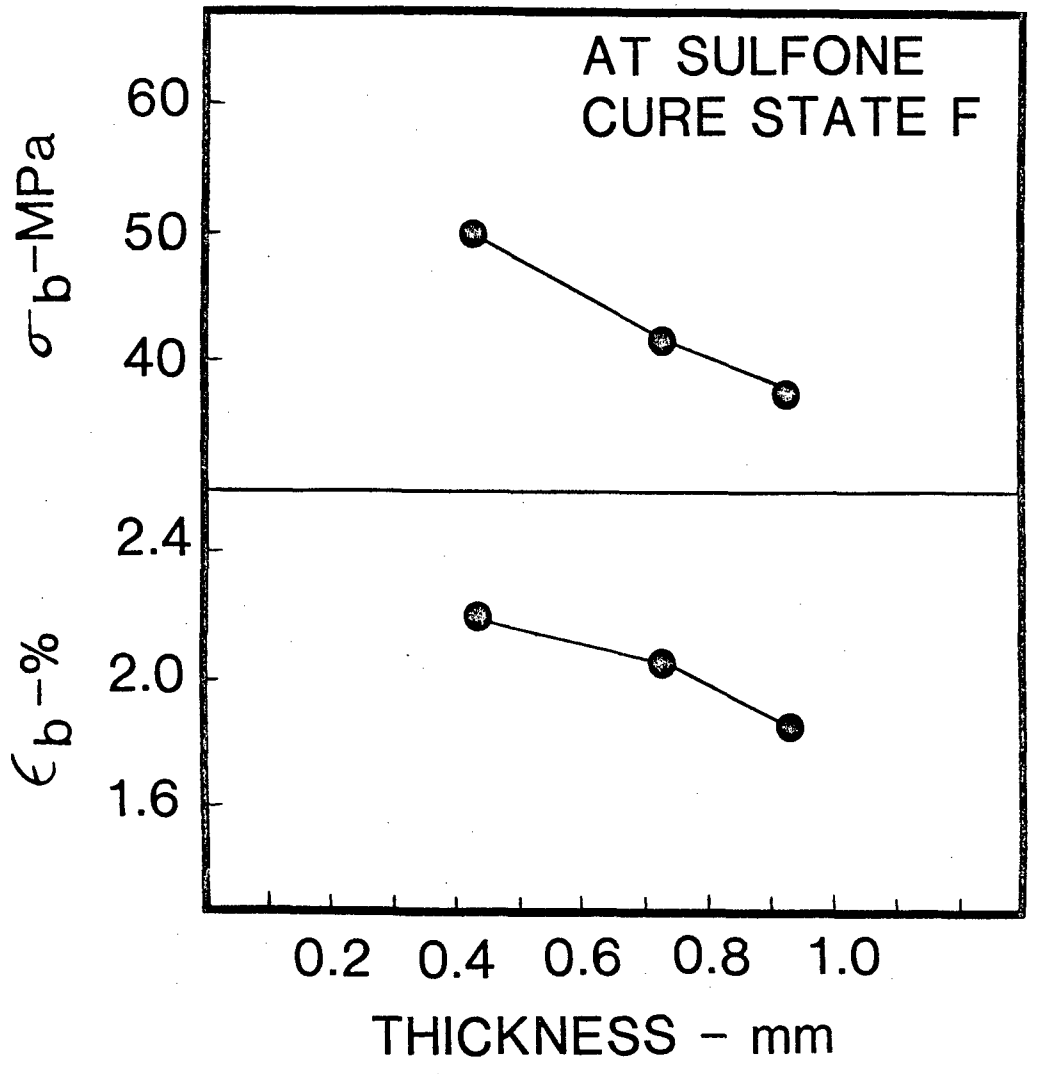

Figure 7. Sample Thickness Effect on Tensile Properties

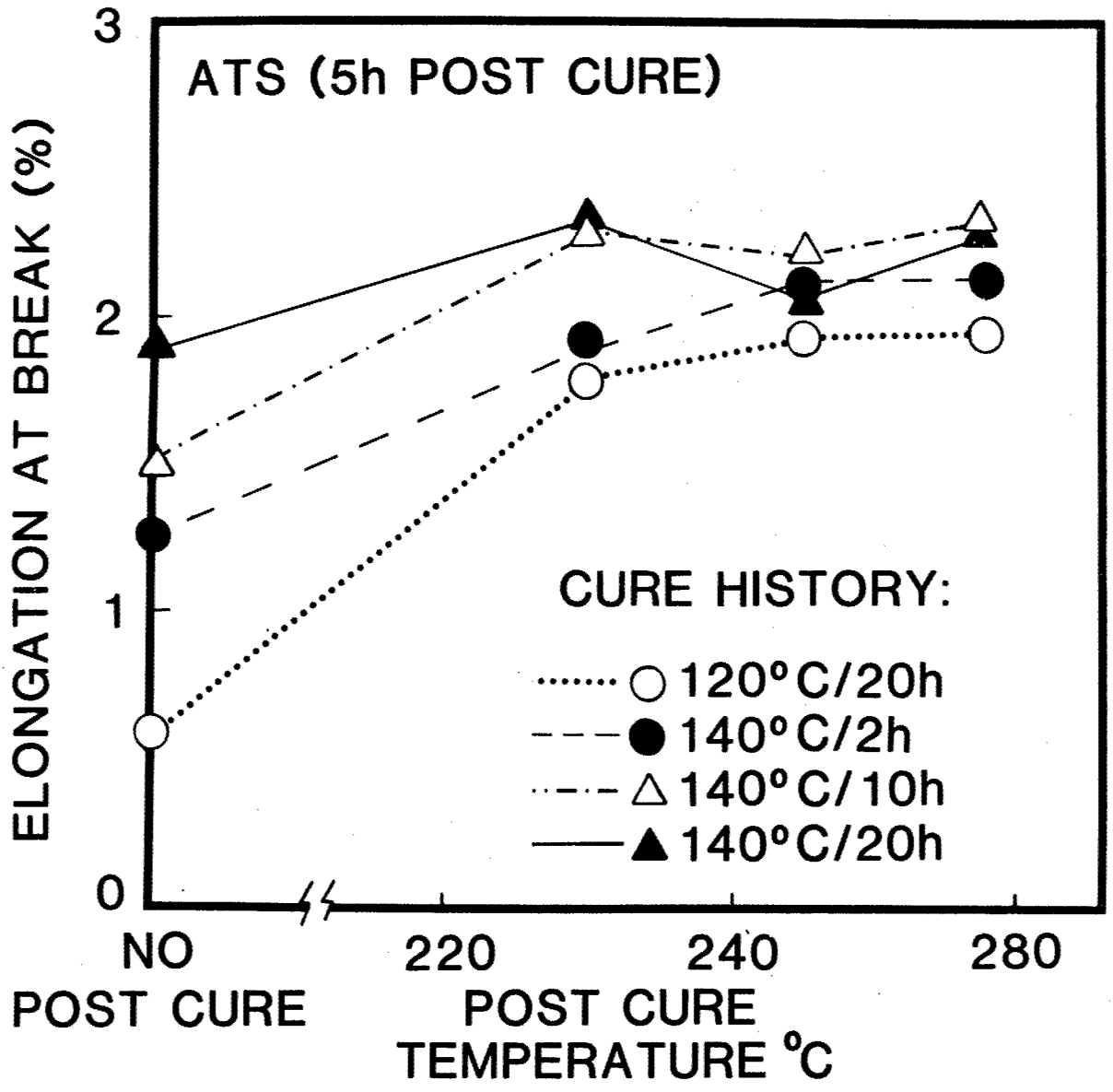

Figure 8. Cure Time Effect on Tensile Properties

delaminate when they were removed from the autoclave (Reference 11). This can be explained by the fact that the samples were perturbed before adequate properties was developed to handle the stress and strain induced by the thermal shrinkage. This may be avoided by redesigning the cure schedule to account for the properties before the post cure.

Figure 9 shows the post cure temperature effect on the elongation at break. The values are plotted as a function of post cure temperature. All specimens were post cured for 5 hours. Each curve in the plot shows a certain precure history. For a given precure history, there is no significant effect from the post temperature within the range between 220°C to 280°C.

The data without post cure show a definite trend of improvement with properties with increasing extent of cure. The post cure data also show a slight trend of improvement with increasing extent of precure. This is in disagreement with the recent fracture energy data on ATS reported by Rockwell International (Reference 12) which indicate that the fracture energy increases when the extent of low temperature cure is smaller. This disagreement deserves further investigation.

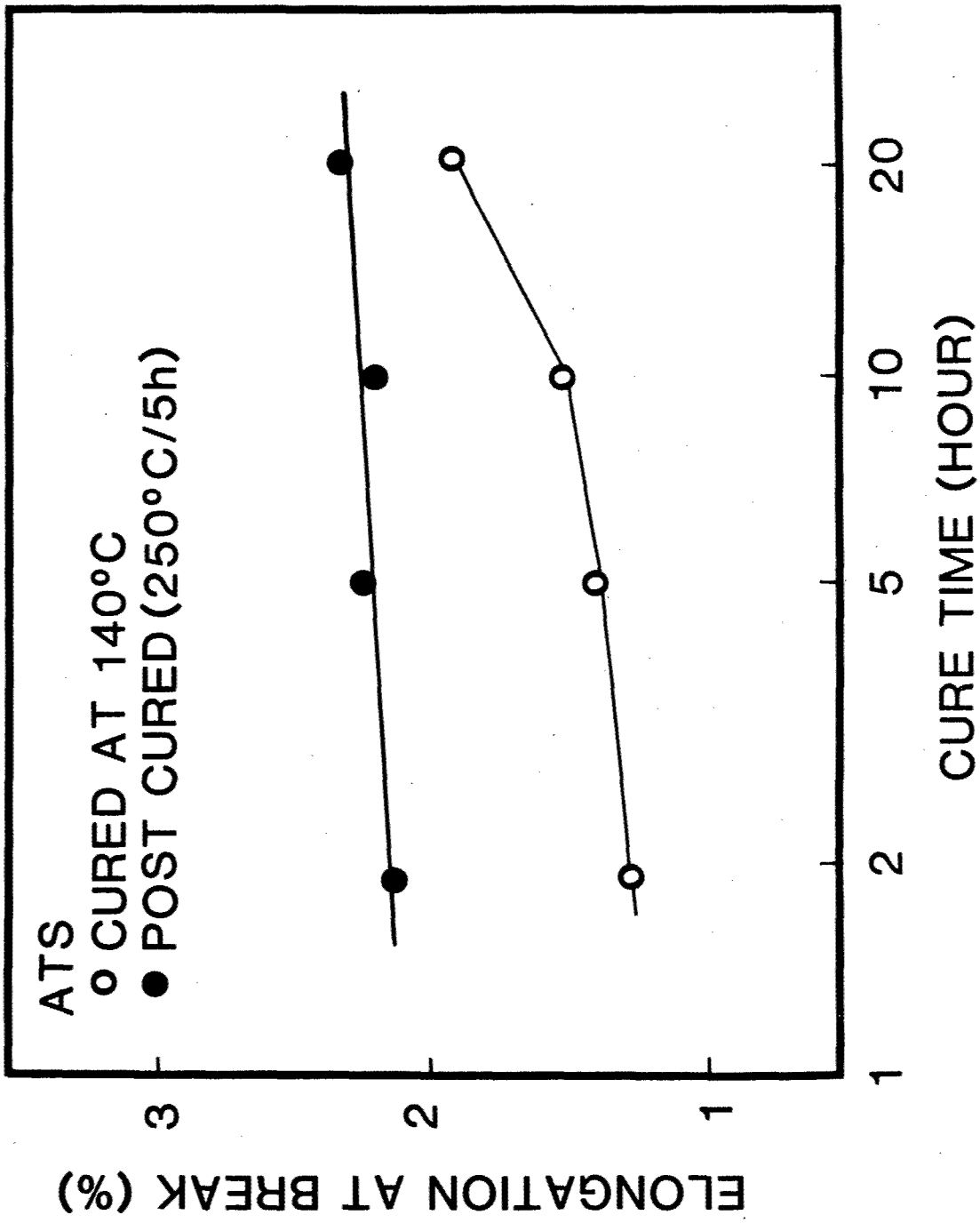

Figure 9. Post Cure Temperature Effect on Tensile Properties

SECTION IV

CONCLUSIONS

The study has shown that air curing of acetylene terminated sulfone resin can improve its mechanical properties. Whether this is a general characteristic of all acetylene terminated resins, or the observed effect is unique with the sulfone resin will have to await further studies.

The data appear to support the notion that curing in air can influence network structure. Oxygen may have been incorporated in the cured structure.

Sample thickness as well as the sequence of air exposure can influence the amount of mechanical improvement. These are factors that should be taken into consideration when designing proper processing conditions for the resin.

Data showing mechanical properties of the resin before it was fully cured suggested the importance of such data in choosing the proper cure schedule so that appropriate precaution can be taken to avoid predamaging the fabricated parts during the processing procedure.

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